Molybdenum cell for x-ray diffraction measurements of fluid alkali metals at high temperatures and high pressures

AUTHOR(S):

Matsuda, K; Tamura, K; Katoh, M; Inui, M

CITATION:

Matsuda, K ...[et al]. Molybdenum cell for x-ray diffraction measurements of fluid alkali metals at high temperatures and high pressures. REVIEW OF SCIENTIFIC INSTRUMENTS 2004, 75(3): 709-712

ISSUE DATE:

2004-03

URL:

http://hdl.handle.net/2433/50127

Molybdenum cell for x-ray diffraction measurements of fluid alkali metals at high temperatures and high pressures

Kazuhiro Matsuda[a] and Kozaburo Tamura
Department of Materials Science and Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Masahiro Katoh
Material Research Department, Allied Material Corporation, Iwasekoshi-Machi 2, Toyama 931-8543, Japan

Masanori Inui
Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

(Received 27 October 2003; accepted 15 November 2003)

We have developed a sample cell for x-ray diffraction measurements of fluid alkali metals at high temperatures and high pressures. All parts of the cell are made of molybdenum which is resistant to the chemical corrosion of alkali metals. Single crystalline molybdenum disks electrolytically thinned down to 40 μm were used as the walls of the cell through which x rays pass. The crystal orientation of the disks was controlled in order to reduce the background from the cell. All parts of the cell were assembled and brazed together using a high-temperature Ru–Mo alloy. Energy dispersive x-ray diffraction measurements have been successfully carried out for fluid rubidium up to 1973 K and 16.2 MPa. The obtained $S(Q)$ demonstrates the applicability of the molybdenum cell to x-ray diffraction measurements of fluid alkali metals at high temperatures and high pressures.
 [DOI: 10.1063/1.1646769]

I. INTRODUCTION

A considerable amount of theoretical or experimental works have been given to investigate the physical properties of fluid metals over a wide range of temperature and pressure. Much attention has been paid to those in the critical region, where various phenomena particular to fluid metals appear.[1] The metal–nonmetal (M–NM) transition observed around the critical region is a marked phenomenon, which distinguishes metallic fluids from normal insulating fluids.[2]

Fluid alkali metals are typical examples of materials whose physical properties are strongly dependent on the thermodynamic state. Liquid alkali metals near the triple point are generally regarded as simple monatomic liquids with their physical properties resembling those of the solid state. The transport properties such as electrical conductivity are well explained within the framework of nearly-free-electron model. However, the deviation from the model appears when the density of the liquids decreases.[3] When the fluids are expanded further by heating up to the critical point, the conductivity substantially decreases and eventually the M–NM transition occurs, which implies a drastic variation in the nature of the interatomic interaction as indicated by the conductivity data of rubidium (Rb)[4] and cesium (Cs).[5]

It is interesting to investigate the interrelation between the electronic and the structural properties in the M–NM transition region. Several structural studies on expanded fluid alkali metals at a high temperature region have been carried out. Franz *et al.*[6] performed neutron diffraction experiments of Rb up to 2000 K. Winter *et al.*[3] also carried out the neutron diffraction of Cs up to its critical region. Diffraction measurements using synchrotron radiation have also been carried out. Hosokawa *et al.*[7] performed x-ray diffraction experiments of Rb up to 1573 K using a sample cell made of single crystalline sapphire. The precision of the data was significantly improved by the use of synchrotron radiation. However, the temperature range was limited to 1573 K due to the reactivity of alkali metal with sapphire.

Molybdenum is known to be resistant to chemical corrosion with alkali metals and widely regarded as a suitable material for those experiments at high temperatures exceeding the critical temperatures ($T_c = 2017$ K for Rb and $T_c = 1924$ K for Cs) to measure the equation of state,[8] electrical conductivity,[8] and also the neutron diffraction.[6] The use of a molybdenum cell for x-ray diffraction measurements of fluid alkali metals is quite attractive because it enables us to investigate the structural changes accompanying the M–NM transition in the supercritical region. In addition, combined with a synchrotron radiation as an x-ray source, more precise data on the structural changes might be obtained.

In the present article we report the design and the fabrication of a new sample cell made of molybdenum for x-ray diffraction measurements using synchrotron radiation.

II. MOLYBDENUM CELL

A. Construction of the cell

Figure 1(a) illustrates the construction of a sample cell. The cell was designed for x-ray transmission geometry and all parts of which were made of molybdenum. The cell mainly consists of three components, an outer pipe which is indicated by (1) in the figure (4 mm in outer diameter and 3

[a]Electronic mail: matsuda@mtl.kyoto-u.ac.jp

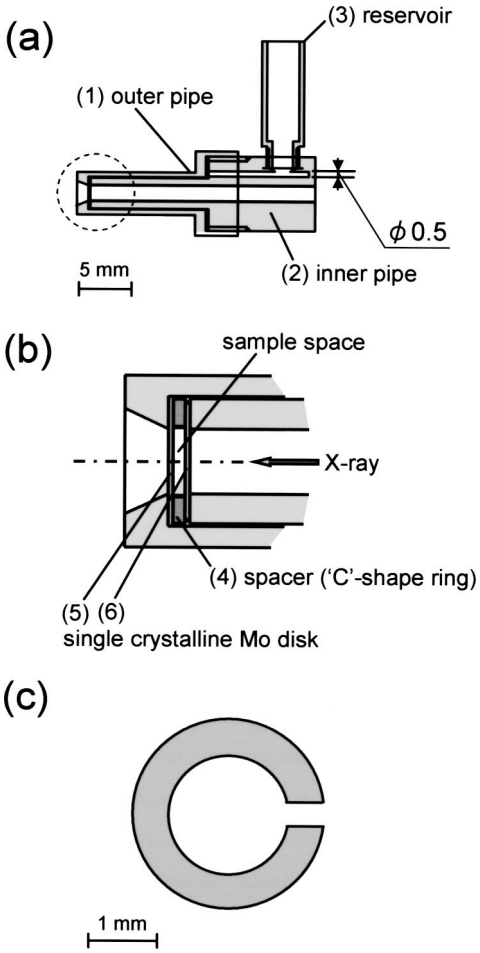

FIG. 1. (a) The construction of a sample cell made of molybdenum, (b) the enlargement of the area enclosed with the broken circle in (a), and (c) a C-shape ring spacer.

mm in inner diameter), an inner pipe (2) (3 mm in outer diameter and 1.5 mm in inner diameter), and a reservoir (3). These three components were made of polycrystalline molybdenum and were all fabricated with conventional machining techniques. They were screwed together with each other and then sealed with high temperature Ru–Mo brazing alloy. The hole with 0.5 mm in diameter in the inner pipe shown in the figure was made by electrodischarge machining and made for introducing liquid sample in the reservoir into the area enclosed with the circle in Fig. 1(a).

Figure 1(b) shows an enlargement of the area enclosed with the circle in Fig. 1(a). A spacer (4) with thickness of 0.4 mm made of polycrystalline molybdenum, which is shown in Fig. 1(c) and called ''C''-shape ring, determines the sample thickness and was located between two thinned walls made of single crystalline molybdenum with thickness of 40 μm [(5),(6)]. The liquid sample contained in the reservoir is introduced into the sample space through the hole with 0.5 mm in diameter and the narrow path between two pipes. The C-shape of the ring spacer is in order for facilitating the introduction of the liquid sample into the sample space.

The incident x rays come from the right-hand side as indicated by the arrow in Fig. 1(b). The x rays scattered by the fluid sample and molybdenum walls go out to the direction of the left-hand side. The left end was tapered for outgoing x rays with large scattering angles so as to pass without blocking.

B. Single crystalline molybdenum

The most important point in the cell construction is the use of the single crystalline molybdenum as the material for the walls of the cell indicated by (5) and (6) in Fig. 1(b).

We have so far performed energy dispersive x-ray diffraction measurements for expanded fluid Hg and Se at the supercritical conditions using a high pressure vessel specially designed in our laboratory.[9–11] The vessel has pressure-sealed beryllium (Be) windows located at different angles of 2θ (4°,7°,11.5°,15°,20°,25°,33°) through which scattered x rays go out and are detected by a pure germanium solid state detector (a pure Ge SSD). This construction is quite effective for the measurements at high pressures and high temperatures. We have successfully obtained the precise structural data on expanded fluid Hg and Se at the supercritical conditions.[10]

In the energy-dispersive method white x rays are used as the incident beam, so polycrystalline molybdenum could not be used because x rays scattered by the polycrystal produce a huge background including a Debye–Scherrer pattern disturbing the signals from the fluid sample. In the present experiment, we used single crystalline molybdenum disks for the walls of the cell through which x rays pass as indicated by (5) and (6) in Fig. 1(b). The diffraction spectrum might contain the Bragg peaks from the cell. We could remove the Bragg peaks in the spectrum by controlling the crystal orientation as described later.

Since the main oscillations of the structure factor $S(Q)$ of liquid Rb[6] near the melting point appear at a lower Q region than those of liquid Hg,[10] it is important to choose the crystal axis of molybdenum which gives no Laue spots in the region of small angles of 4°, 7°, and 11.5°. We carried out the simulation of the Laue patterns from molybdenum crystal when the incident x rays are scattered from the wall of the cell. We found that the selection of the crystal axis with low Miller index such as ⟨100⟩, ⟨110⟩, and ⟨111⟩ is appropriate. In the present experiments, we adopted the axis with ⟨100⟩ index.

In addition, it is important to reduce the thickness of molybdenum disk for obtaining sufficient intensity of the scattered x rays from the fluid sample. This is crucial when the density of the fluid approaches that in the critical region where the signal becomes quite weak. In the present experiment, we have successfully fabricated the disk with thickness of 40 μm. The thinned disk was made by the following procedure. The backscattering Laue method was employed for determining the crystal orientation of a bulk single crystal made by a technique of crystal growth in the solid state of a polycrystal.[12] The disks with a thickness of about 250 μm were cut down from the crystal using an electrodischarge method. The disks were mechanically polished down to 100 μm and then electrolytically etched to 40 μm using methanol–H_2SO_4 (volume fraction 7:1) solution.

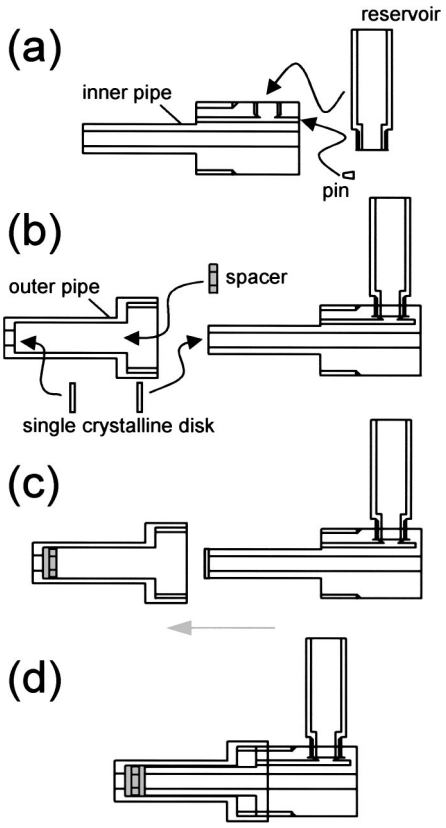

FIG. 2. The assembling procedure of the molybdenum cell at each step [(a)–(d)]. The components were brazed with each other using the high temperature brazing alloy of 43 wt % Ru–Mo powder.

C. Assembling and brazing

After all the parts of the cell (an outer pipe, an inner pipe, a reservoir, two single crystalline disks, and a C-shape ring) were prepared, they were connected with each other by brazing in a furnace using 43 wt % Ru–Mo alloy as a brazing metal.[13]

First, an inner pipe and a reservoir were screwed to each other and the end of the hole with 0.5 mm in diameter was sealed with a small molybdenum pin as shown in Fig. 2(a). Then the brazing metal was applied into the connected area between these components and a brazing process was carried out at 2000 °C for 5 min in the vacuum (10^{-3} Pa) followed by the cooling process in the furnace. The rate of the temperature increase was 10 °C/min. In this process, the brazing metal melted and the components were connected. Second, a single crystalline disk and a spacer were inserted into the outer pipe and positioned at the end. Another single crystalline disk was set on the end of the inner pipe. The brazing metal was applied into the contact area of each component and the brazing at the same condition was performed [Fig. 2(b)]. Finally, the two pipes were screwed to each other and the brazing metal was applied into the connected area. The brazing was carried out again [Figs. 2(c) and 2(d)]. After each step of the brazing process was finished, the seal around the connected area was examined with a helium (He) leak detector. In each step the same brazing process was repeated until no leakage is found.

Figure 3 shows the fabricated molybdenum cell in (a) and the transmission Laue pattern in (b) obtained by using an in-house white x-ray source operated at 46 kV, 16 mA. Laue spots with fourfold symmetry are clearly observed, which confirms that the crystal axis of the cell corresponding to ⟨100⟩ orientation is well accomplished. Two nearby spots seen in Fig. 3(b) correspond to those separately coming from two single crystalline molybdenum disks kept at distance with the inserted C-shape ring spacer. The sharp Laue spots show that no mechanical strains are introduced into the disk throughout the fabrication process of the cell.

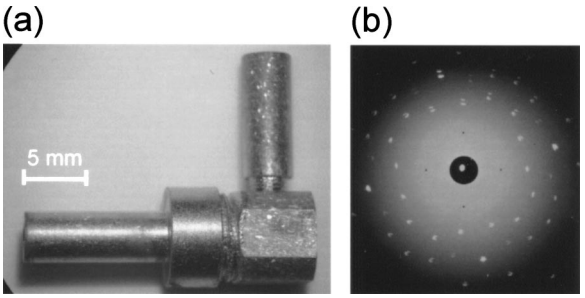

FIG. 3. (a) The fabricated molybdenum cell. (b) The transmission Laue diffraction spots from the two single crystalline molybdenum disks used as the walls of the cell.

III. DIFFRACTION EXPERIMENTS

Liquid Rb was introduced into the cell in a glove box filled with highly purified He gas. In the glove box, first, we put a small vacuum chamber within which a small furnace was installed for heating the cell. Solid Rb was put in the reservoir of the cell and the cell was set in the chamber, and then the chamber was evacuated. Next, the cell was heated up above the melting temperature of Rb (39 °C). After the melting of Rb in the reservoir was confirmed, the chamber was leaked in the glove box and He gas was introduced into the chamber. The surface of liquid Rb in the reservoir was forced with He gas and then the liquid sample was introduced into the sample space through the hole with 0.5 mm diameter and the narrow path between two pipes as shown in Fig. 1(a). Finally, the molybdenum cell filled with Rb was put in the high pressure vessel and the vessel was closed, the procedure of which was carried out in the glove box. Then the vessel was taken out of the glove box.

Energy-dispersive x-ray diffraction measurements for fluid Rb were performed on the beam line (BL28B2) at SPring-8. White x rays were used as the incident beam, and scattered x rays were detected by a pure Ge SSD. Figure 4 shows the raw spectra at angle $2\theta=4°$ obtained by the measurements at several temperatures and pressures up to 1973 K, 16.2 MPa. We have also succeeded in obtaining the spectrum at 1973 K, 9.5 MPa, which corresponds to that in the dense vapor phase. These data are those obtained after the escape correction of a pure Ge SSD.[9] The first maximum was observed clearly at 45 keV, which corresponds to the first peak of the structure factor $S(Q)$ of liquid Rb. Data analysis to obtain $S(Q)$ from the spectrum requires further data corrections in addition to the escape effect of the a pure Ge SSD, such as the energy spectrum of the incident x-ray beam, the effect of the absorption by the molybdenum cell,

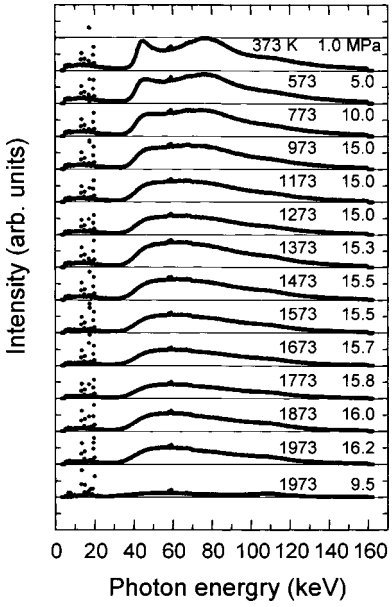

FIG. 4. The diffraction intensity vs photon energy for fluid Rb at various temperatures and pressures.

compressed He gas, the Be windows, the fluid Rb sample itself, and finally the Compton scattering of the sample and the cell.[14]

In Fig. 5 we show $S(Q)$ for fluid Rb obtained at three different temperatures and pressures. Dots represent the experimental data. At 373 K the position of the first maximum is located at 15.2 nm^{-1} showing good agreements with the data obtained by the others.[15,16] The overall shape of $S(Q)$ also coincides well with the previous data,[15,16] showing the reliability of our data obtained by using the molybdenum cell. With increasing temperature, the oscillation of $S(Q)$ is damped. The intensity of the first maximum is strongly reduced and the shape of the peak is broadened with increasing temperature and with decreasing density, which also shows the same tendency previously observed in expanded fluid Rb[6] and Cs.[3]

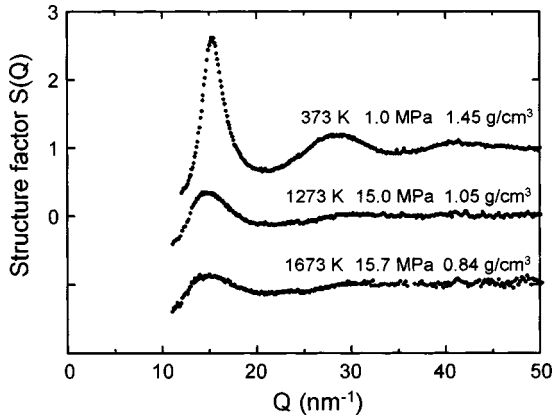

FIG. 5. Structure factor $S(Q)$ for fluid Rb at three different temperatures and pressures.

Further discussion on the results of the data analysis is beyond the scope of this paper and it will be given in later publications.

ACKNOWLEDGMENTS

The authors would like to express our gratitude to Y. Ito for valuable supports for the fabrication of the cell. The authors are also grateful to Professor K. Osamura, Professor Y. Hiraoka, Dr. K. Ito, and Professor M. Yamaguchi for valuable suggestions on the cell preparation. The authors thank H. Ito, M. Kusakari, K. Sato, K. Mifune, and K. Kato for their helpful support on the diffraction experiments at SPring-8. This work was supported by a Grant-in-Aid for Scientific Research Fund from the ministry of Education, Culture, Sports, Science and Technology (Specially Promoted Research No. 11102004). One of the authors (K.M.) would like to acknowledge the Japan Society of Promotion of Science. The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2003A6020-LD-np).

[1] F. Hensel and W. W. Warren, Jr., *Fluid Metals; Liquid-Vapor Transition of Metals* (Princeton University Press, Princeton, NJ, 1999).
[2] F. Hensel, Ber. Bunsenges. Phys. Chem. **80**, 786 (1976).
[3] R. Winter, F. Hensel, T. Bodensteiner, and W. Gläser, Ber. Bunsenges. Phys. Chem. **91**, 1327 (1987).
[4] W. Freyland, Comments Solid State Phys. **10**, 1 (1981).
[5] F. Hensel, M. Stoltz, G. Hohl, R. Winter, and W. Götzlaff, J. Phys. Colloq. **C5**, 191 (1991).
[6] G. Franz, W. Freyland, W. Gläser, F. Hensel, and E. Schneider, J. Phys. Colloq. **C8**, 194 (1980).
[7] S. Hosokawa, W.-C. Pilgrim, F. Hensel, J.-L. Hazemann, D. Raoux, M. Mezouar, T. Le Bihan, and D. Häusermann, J. Non-Cryst. Solids **250–252**, 159 (1999).
[8] H. P. Pfeifer, W. Freyland, and F. Hensel, Ber. Bunsenges. Phys. Chem. **83**, 204 (1979).
[9] K. Tamura, M. Inui, and S. Hosokawa, Rev. Sci. Instrum. **70**, 144 (1999).
[10] K. Tamura and M. Inui, J. Phys.: Condens. Matter **13**, R337 (2001).
[11] K. Tamura, M. Inui, I. Nakaso, Y. Oh'ishi, K. Funakoshi, and W. Utsumi, J. Phys.: Condens. Matter **10**, 11405 (1998).
[12] K. Okamoto, M. Mori, T. Fujii, and Y. Hiraoka, in *Proceeding of the 12th International Plansee Seminor '89*, edited by H. Bildstein and H. M. Ortner (Reutte, Tirol, Austria, 1989), pp. 171–184.
[13] Y. Hiraoka and T. Fujii, in *Proceeding of the 12th International Plansee Seminor '89*, edited by H. Bildstein and H. M. Ortner (Reutte, Tirol, Austria, 1989), pp. 265–279.
[14] S. Hosokawa, T. Matsuoka, and K. Tamura, J. Phys.: Condens. Matter **3**, 4443 (1991).
[15] Y. Waseda, *The Structure of Non-Crystalline Materials; Liquids and Amorphous Solids* (McGraw-Hill, New York, 1980).
[16] M. S. Zei, Phys. Rev. B **24**, 4509 (1981).